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S. W. STRATTON, Director

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## DETERMINATION OF SULPHUR IN ILLUMINATING GAS

BY

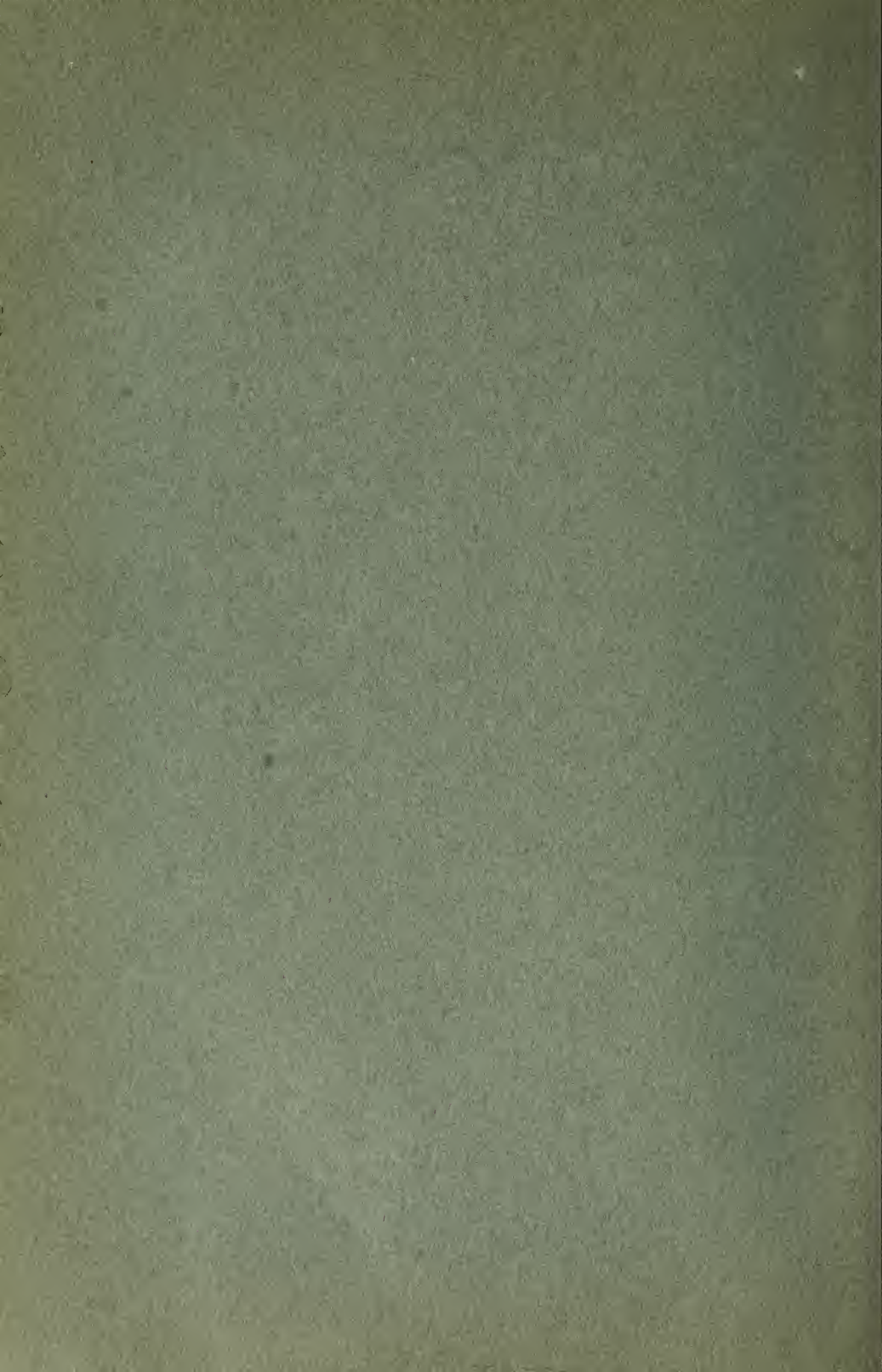R. S. McBRIDE, Assistant Chemist
and
E. R. WEAVER, Laboratory Assistant
*Bureau of Standards*

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## By R. S. McBride and E. R. Weaver

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## I. APPARATUS AND METHODS EMPLOYED

The methods for determination of sulphur in gaseous fuels can be classified into four groups, the general principles of which are as follows:

1. The gas is burned and the sulphur oxides in the products of combustion are condensed or absorbed, oxidized to sulphate, and determined as such.

2. The sulphur compounds are oxidized by liquid reagents giving the sulphate, which can be determined directly.

3. The sulphur compounds are oxidized by burning the gas, but the sulphur is absorbed and determined as sulphur dioxide.

4. The sulphur compounds are reduced to give hydrogen sulphide, which is then absorbed and determined.

The methods of group 1 have been most used in American practice and are generally considered the most accurate and convenient, either for works control or official testing. Five distinct forms of apparatus of this general class and some variations of them have been tried, and the report of these tests is given in detail in the following sections. In these investigations the relative accuracy and convenience of the various forms were considered with the idea of determining the best conditions for operation of each. In describing our experience with these apparatus some of the points are discussed in detail in order to assist inexperienced operators to a rather full understanding of the reasons for some precautions and directions given.

The methods of groups 2 and 4 are probably least used, and they are also perhaps subject to the greatest inaccuracies, since in either the wet oxidation or the reduction to hydrogen sulphide it seems certain that not all of the sulphur in various kinds of gas is completely oxidized or reduced, so that the results are too low. The few tests made on these methods gave very unsatisfactory results. In the case of the method of reducing to hydrogen sulphide the deposition of large amounts of carbon on the catalyzer was a constant source of difficulty.

The methods of group 3, particularly the method of Somerville, have been used to some extent, and it appears probable that a modification of the Somerville method could be used, if desired, for rapid and approximate determination in works control. Brief attention is given to such a method on page 12.

### 1. REFEREES APPARATUS

The apparatus most often used in this country for official or works control determination of total sulphur is that of the Metropolitan Gas Referees, specified for official use in London. This

apparatus is described as follows in the Notification of the Gas Referees for the Year 1913:

The gas is burnt in a small Bunsen burner with a steatite top, which is mounted on a short cylindrical stand perforated with holes for the admission of air and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of a glass trumpet tube. There are both in the side and in the top of this stand 14 holes of 5 millimeters in diameter, or an equivalent airway. On the top of the stand, between the narrow stem of the burner and the surrounding glass trumpet tube, are to be placed pieces of commercial sesquicarbonate of ammonia, weighing in all about 2 ounces.

The products both of the combustion of the gas and of the gradual volatilization of the ammonia salt go upward through the trumpet tube into a vertical glass cylinder with a tubulure near the bottom, and drawn in at a point above this to about half its diameter. From the contracted part to the top the cylinder is packed with balls of glass about 15 millimeters in diameter to break up the current and promote condensation. From the top of this condenser there proceeds a long glass pipe or chimney tube slightly bent over at the upper end, serving to effect some further condensation, as well as to regulate the draft and afford an exit for the uncondensable gases. * * * In the bottom of the condenser is fixed a small glass tube, through which the liquid formed during the testing drops into a flask placed beneath. * * * The lower end of this tube is contracted so that when in use it may be closed by a drop of water.



Fig. 1.—*Referees Apparatus*

In the apparatus first used by us the top of the trumpet tube was introduced into the tubulure of the condenser, a tight joint being made by a thin rubber stopper. But our experience showed that a rubber connection of any kind at this point is undesirable, since the upper end of the trumpet tube becomes very hot and sulphur may be introduced into the apparatus from the rubber. The first time a new rubber connection was used on such an apparatus it caused an error of 60 per cent in the sulphur found A ground-glass connection at this point would be the best except for its fragility; but a soft, well-fitting cork was found to make a tight connection when used in either of two ways. If the tubulure and trumpet tube are about the same size, Fig. 2a shows the simplest method of connection; if the trumpet tube is consider-
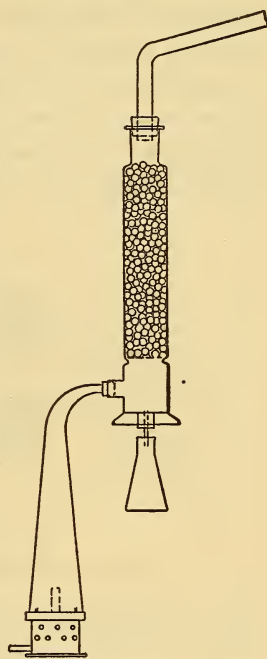
ably smaller than the tubulure, as is the case with the apparatus sold by some makers, connection can be made as in Fig. 2b.

As has been already stated, the use of a rubber connector as illustrated in the "Notification" of the London referees, or substitution of rubber for cork in the form of Fig. 2b is not desirable.

It is best to allow the small glass outlet tube at the base of the condenser to project slightly above the rubber stopper which holds it, in order that the stopper may be protected from the hot gases by a layer of liquid.

A perforated lead plate, to be used at the bottom of the condenser as a support for the glass marbles, is furnished with the apparatus by one dealer. This should be replaced by a porcelain or glass plate or by a support made of glass rod bent to S shape.
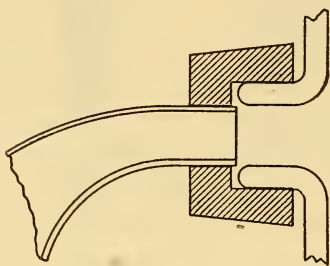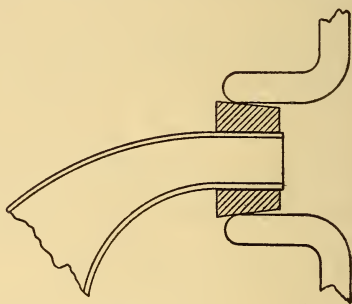
Fig. 2a                                    Fig. 2b

*Connection of Trumpet Tube and Condenser in Referees Apparatus*

The lead plate would always be likely to cause errors in the determination of the sulphate, and would certainly do so during the first few runs while a film of lead sulphate was forming over the metal surface. When setting up the apparatus, it is best to fill the condenser cylinder with water, so that the marbles may be dropped in without danger of breaking it.

Two condensers of different shapes, representing the forms furnished by two different dealers in apparatus, were used at this Bureau, the space occupied by marbles in one having an internal diameter of 6 cm and a height of 30 cm, in the other of 7 and 18 cm, respectively. Although differing by about 25 per cent in size, the two gave practically the same efficiency of condensation, judging by the values obtained. (See comparison of

Table 1.) At the beginning of the tests made with them the two models were run practically as specified in the 1912 "Notification," above refereed to. Large pieces of ammonium carbonate, freed from efflorescent portions, were placed about the burner stem and the gas was lighted. After burning long enough to purge the meter and connections, the trumpet tube was slipped over the burner and connected with the condenser quickly, the meter reading being noted at the instant when the connection was made; and the gas was burned at 0.4 to 0.6 cubic feet per hour for the desired period (from 2 to 8 hours). At the end of this time the apparatus was allowed to cool and then rinsed in the following manner: The trumpet and chimney tubes were first disconnected from the condenser and each was rinsed once; then the tubulure of the condenser was closed by a stopper and the marbles were rinsed with three portions of water of about 50 cc each, the portions of wash water being poured into the top of the condenser quickly in order to flush all the surfaces of the marbles. All washings and the condensed liquid obtained during the test were combined and the sulphate was determined as barium sulphate by the method described in a later section. No correction for pressure or temperature was necessary, since all tests at any one time were run under the same conditions and only comparative values were needed.

Variations from this general procedure, which were made from time to time to investigate the effect of these changes upon the results, will be indicated in the report of the results later.

### 2. ELLIOTT APPARATUS

The original form of Elliott apparatus, illustrated in Fig. 3, has been used to some extent; but in most cases it is being replaced, as it has been found too fragile for ordinary use. In referring to the later form of apparatus, which is illustrated in Fig. 4, Dr. Elliott [1] says: "This is the latest modification of sulphur apparatus and is the one we prefer to use, because it is less fragile than the ones formerly used, which were readily broken." Because of the infrequency of its use only a few tests were made upon the older form of apparatus.

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[1] Private communication to this Bureau.

The new form devised by Dr. A. H. Elliott has not been fully described by him in any publication, only a brief reference to it being found in Baskerville's Municipal Chemistry (p. 319). Fig. 4 shows the form preferred by the originator, as given to the Bureau in a private communication. The porcelain Bunsen burner, with a perforated porcelain plate near the top, supports pieces of ammonium carbonate. A trumpet tube resting on the plate conveys the products of combustion mixed with ammonia to the top of the first condenser (a 24-inch calcium chloride tower). The tubulure at the bottom of this cylinder is connected with that of the second cylinder of the same kind. Glass tubes drawn down to small tips are fitted into rubber stoppers in the bottom of each tower, allowing the condensate to drip into flasks placed beneath.

The apparatus as designed by Dr. Elliott had a rubber adapter at the top of the short trumpet tube, connecting it with the bent tube leading to the first condenser. This rubber connection should be removed and the two tubes sealed together to prevent sulphur being introduced from the rubber. A well-fitting cork stopper serves to connect the trumpet tube to the condenser, and as the gases are well cooled before reaching the bottom of the tower the use of a rubber connection at that place is permissible. As can be seen from the figure, the principle and general form of the apparatus is similar to that of the Referees.

Fig. 3.—*Old Model Elliott Apparatus*

The new-form Elliott apparatus was operated in the same general manner as the Referees, the principal changes being in rate

of burning of the gas and amount of water required for washing. The gas was burned usually at from 0.7 to 1 cubic foot per hour.

The older form of Elliott apparatus (Fig. 3 above) requires the use of water to cool the bulb condenser. Two methods of introducing the alkali for absorbing the sulphur oxides are available: First, use of ammonium hydroxide or ammonium carbonate at



Fig. 4.—*New Model Elliott Apparatus*

the burner, as in the Referees or Hinman-Jenkins apparatus; and, second, use of alkaline solutions run in at the top of the condenser. For the first comparisons made (see Table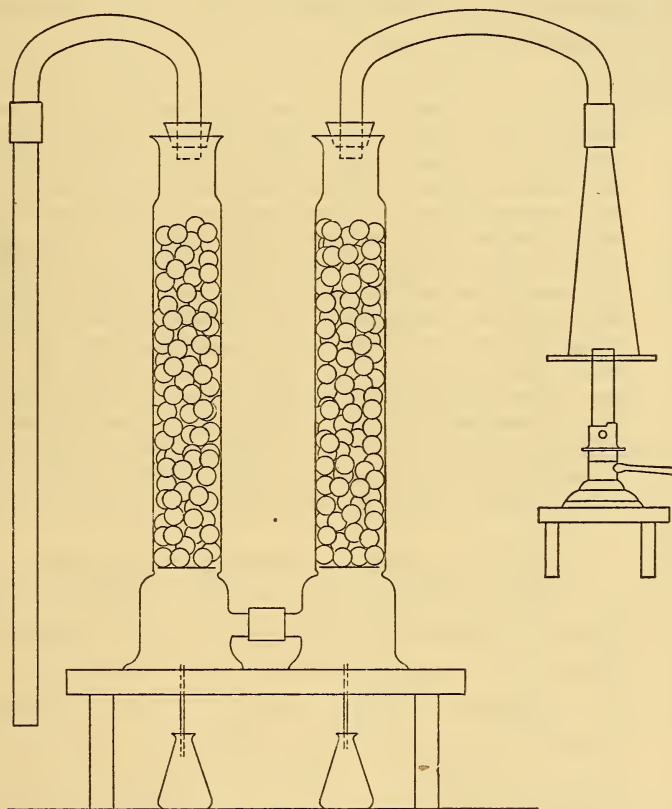 2) sodium hydroxide was run in at the top of the condenser; but the presence of volatile alkali was found necessary, and for the later tests ammonium carbonate about the burner was found most convenient. The gas

was burned at the rate of 0.4 to 0.6 foot per hour and the washing of the condenser accomplished with about 200 to 300 cc of water, as in the case of the Referees apparatus.

### 3. HINMAN-JENKINS APPARATUS

The apparatus, known by the names of its inventors as the Hinman-Jenkins form, is illustrated in Fig. 5. It is described by Jenkins [2] in the following words:

The upper vessel is a "bead glass" 300 mm long and 60 mm in diameter; this is filled with large cut-glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm long and 50 mm lower internal diameter. To the upper adapter is attached, by means of the "connecting piece," the lower adapter, 400 mm long and 40 mm lower diameter. The connecting piece projects 12 mm above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm hole; surrounding the burner is a glass tube 20 mm in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm in diameter. Into this chamber, which serves to contain 10 per cent ammonium hydroxide, the lower adapter dips 10 mm.
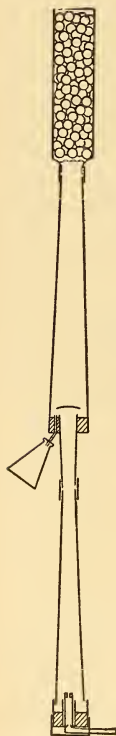
The lower adapter is joined to the "connecting piece" by a short cork-lined metal tube. Although radically different in form, this apparatus is very similar to the Referees in general principle and in method of use, the principal difference being the use of ammonium hydroxide instead of dry ammonium carbonate as a source of ammonia. About 10 cc of concentrated ammonium hydroxide is placed in the reservoir about the burner at the beginning of the test and about 5 cc more added every 15 or 20 minutes. The gas was burned at the rate of 0.4 to 0.6 cubic foot per hour. When the run was completed the apparatus was allowed to cool and was then flushed four times by pouring 50 cc portions of water in at the top of the bead tube.

Fig. 5.— Hinman-Jenkins Apparatus

[2] Jour. Am. Chem. Soc., **28**, pp. 543–545; 1906.

## 4. DREHSCHMIDT APPARATUS

The original form of the Drehschmidt [3] apparatus, shown in Fig. 6, is used in a few laboratories in this country.

In this apparatus the gas is burned in a metal Bunsen burner under the chimney tube, which rests in a mercury seal, so that all air passing through the apparatus must enter through the air tubes at the base of the burner chamber. This air is drawn in through a tower containing marbles wet with alkali, which prevent entrance of sulphur compounds with the air. The products of
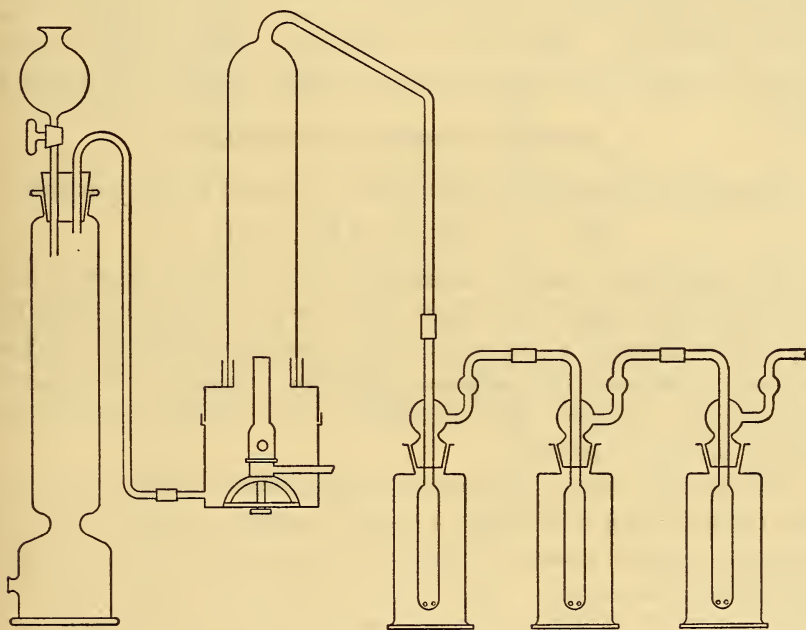


Fig. 6.—*Drehschmidt Apparatus*

combustion are drawn out through the three gas washing bottles, which contain potassium carbonate solution and bromine to condense and oxidize the sulphur oxides.

The gas was burned in this apparatus at about 1 cubic foot per hour and the products of combustion were drawn through the three wash bottles as indicated above. The general procedure described by the originator of this process was followed closely in the use of the apparatus for the few tests made with it.

[3] Chem. Ztg., **11**, p. 1382; 1887.

## 5. MODIFIED DREHSCHMIDT APPARATUS

The majority of the modifications of this apparatus are made almost wholly of glass and are intended for very exact work rather than for works control or official testing.   One of these, which can be put together from simple apparatus to be had in any chemical laboratory, is that described by Harding.[4]   The greatest difficulty met in the use of this latter is that of keeping the burner lighted, as slight fluctuations of air or gas pressure cause it to go out.   To overcome this difficulty a modification of the burner was made and used in an apparatus of somewhat more convenient form than that used by Harding.   This burner, in the form recommended for use where an apparatus of this general group is desired, is shown in Fig. 7.

## 6. MODIFIED SOMERVILLE APPARATUS

The method described by Somerville [5] is based on the reaction:

$$SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$$
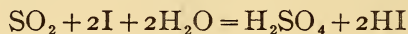
The apparatus consists essentially of a Bunsen burner surrounded by a trumpet tube from which the products of combustion are drawn through a gas wash bottle containing standard iodine solution.   Because the original apparatus seemed unnecessarily complicated, fragile, and expensive the simple modification shown in Fig. 8 was used.

For the first tests 5 g of tenth normal iodine solution was run into the gas wash bottle from a weight burette and diluted to 300 to 400 cc; and the amount of gas burned before the solution became decolorized was noted.   Since it was found that a large error was caused by loss of iodine through volatilization, more iodine was used and a second wash bottle containing a known amount (about 3 g) of tenth normal sodium thiosulphate diluted to 200 cc was added.   Before the iodine solution was entirely decolorized the two solutions were mixed and titrated with one or the other standard solution, depending upon which was in excess, using starch as an indicator.   From the difference between the amount of iodine and thiosulphate used the sulphur contained in the gas was calculated.

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[4] Jour. Am. Chem. Soc., **28**, p. 537; 1906.        [5] Jour. Gas Lighting, **112**, p. 28; 1910.

## II. EXPERIMENTAL PART

To compare the several forms of apparatus, two or more were operated at the same time, being supplied by gas from a common source. The connections from gas supply to meters and from
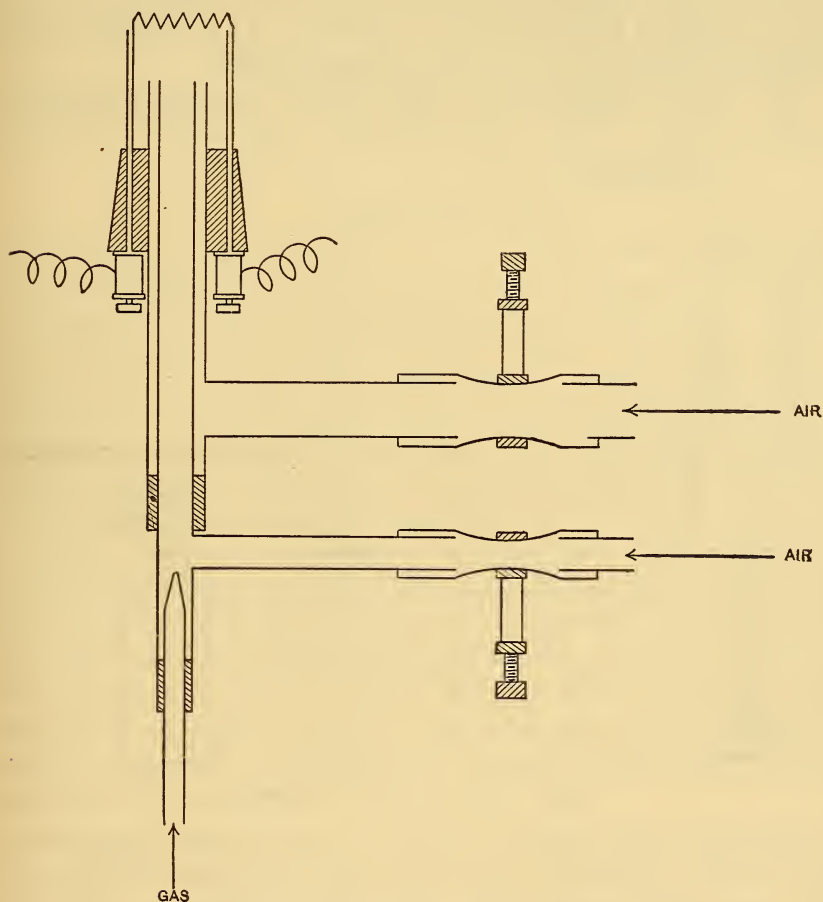


Fig. 7.—*Modified Drehschmidt Burner.*

meters to apparatus were largely of glass, in order that no sulphur should be introduced into or removed from the gas supplied by the rubber tubing and that the possibility of leakage through the tubing would be minimized. To purge each line so that gas of the same character was supplied for each burner, the gas was

burned for a short time before each comparison was begun. It was considered improbable that the difference in rate of passage of the gas through the different meters would cause an appreciable difference in the amount of sulphur compounds which might be taken up by the liquid in the meters; and this is probably the only way in which a difference in the character of gas supplied to the different burners could have been brought about.

The meters employed were filled with 5 per cent glycerin to make changes in water level less rapid. They were run in series
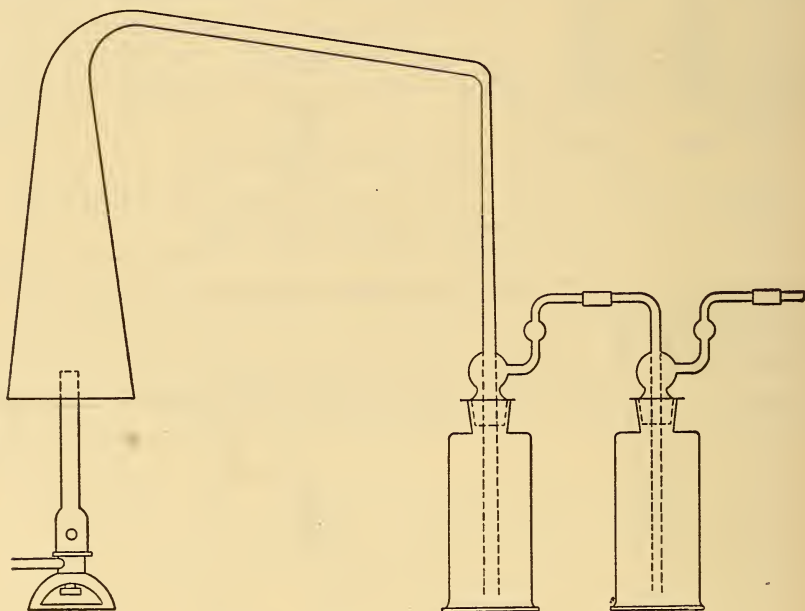


Fig. 8.—*Modified Somerville Apparatus.*

to determine their relative accuracy, in all cases the results showing very fair agreement; and the small corrections indicated by the tests were made upon the observed readings. Frequent recomparison of meters after continued use showed almost exact agreement with the values obtained before use. Very little change in water level was noted over long periods, since the 5 per cent glycerin was taken up by the gas very much more slowly than would have been the case with water. However, for use in ordinary work it is not recommended that meters be filled

with any other liquid than water because of the uncertain solvent action of various solutions upon the gas. For our work, where only relative values were needed, this factor was not of importance.

It was proved that at various rates less than 5 cubic feet per hour the gas became practically equally charged with water on the passage through the meters, so that in cases where two apparatus were run at different rates the gas measurement was not appreciably affected by differences in saturation.

### 1. APPARATUS WITH AIR-COOLED CONDENSERS

#### (a) GENERAL COMPARISONS

A series of comparisons of the Referees, new Elliott, and Hinman-Jenkins apparatus, in which many variations were made to determine the best conditions of operation, the sources of error, etc., is partly summarized in Tables 1 and 2. The results tabulated, however, include only those obtained under normal working conditions and not those obtained when variations were made which would be avoided in practice. The tables give a fair idea of the variations which may be expected in practical operation, as all results thus obtained are included.

Except as otherwise noted, the sulphate in the condensed liquids was determined as barium sulphate by the first method given in Part IV of this paper (p. 33); and except in tests reported in Table 2 no corrections were made for silica. Other gas flames were allowed to burn in the room only when necessary. The error from this latter source is small, because the amount of air taken in by each apparatus was roughly proportional to the amount of gas burned.

## TABLE 1

### Preliminary Comparison of the Referees, Elliott, and Hinman-Jenkins Apparatus

THE GAS BURNED IN THE ELLIOTT APPARATUS AT 0.96 CUBIC FOOT PER HOUR, AND IN THE OTHER THREE AT 0.60 CUBIC FOOT PER HOUR.

| Test | Referees No. 1 (sulphur per 100 cubic feet of gas) | Referees No. 2 (sulphur per 100 cubic feet of gas) | Ratio Referees No. 2 to Referees No. 1 | Elliott (sulphur per 100 cubic feet of gas) | Ratio Elliott to Referees No. 1 | Hinman-Jenkins (sulphur per 100 cubic feet of gas) | Ratio Hinman-Jenkins to Referees No. 1 | Ratio Elliott to Hinman-Jenkins |
|---|---|---|---|---|---|---|---|---|
| | *Grains* | *Grains* | | *Grains* | | *Grains* | | |
| 1 | 13.7 | .......... | .......... | 13.2 | 97.3 | 14.0 | 102.7 | 94.5 |
| 2 | 12.8 | 12.3 | 96.6 | 14.3 | 110.7 | 13.6 | 106.3 | 105.0 |
| 3 | 13.0 | 13.0 | 100.0 | .......... | .......... | 14.2 | 108.9 | .......... |
| 4 | 13.9 | 14.6 | 104.8 | .......... | .......... | 13.2 | 94.5 | .......... |
| 5 | 12.9 | 12.3 | 95.2 | .......... | .......... | 14.2 | 111.9 | .......... |
| 6 | 12.4 | 13.6 | 109.7 | 13.2 | 106.7 | 14.0 | 113.2 | 94.5 |
| 7 | 13.6 | 13.8 | 101.7 | 13.7 | 101.4 | 14.4 | 107.7 | 95.2 |
| 8 | 13.8 | 13.4 | 97.2 | 14.2 | 103.0 | 15.0 | 108.8 | 94.6 |
| 9 | 15.0 | .......... | .......... | 15.2 | 100.8 | 15.9 | 106.1 | 95.5 |
| Average ratio. | .......... | .......... | 100.7 | .......... | 104.5 | .......... | 106.7 | 96.5 |

In the series given in Table 2 all determinations were made in a room free from other flames, and the results were corrected for silica. The results of experiments 18 to 23 show clearly the effect of changing the rate of gas consumption.

## TABLE 2

### Final Comparison, with Gas Burning at Specified Rates, of the Referees, Elliott, and Hinman-Jenkins Apparatus

REFEREES 0.60, ELLIOTT 0.96, HINMAN-JENKINS 0.60 CUBIC FOOT PER HOUR

| Test | Referees No. 1 (sulphur per 100 cubic feet of gas) | Referees No. 2 (sulphur per 100 cubic feet of gas) | Ratio Referees No. 2 to Referees No. 1 | Elliott (sulphur per 100 cubic feet of gas) | Ratio Elliott to Referees No. 1 | Hinman-Jenkins (sulphur per 100 cubic feet of gas) | Ratio Hinman-Jenkins to Referees No. 1 | Ratio Elliott to Hinman-Jenkins |
|---|---|---|---|---|---|---|---|---|
| | *Grains* | *Grains* | | *Grains* | | *Grains* | | |
| 10 | 11.3 | 11.5 | 101.9 | 10.9 | 98.2 | .......... | .......... | .......... |
| 11 | 13.8 | 13.5 | 97.8 | 14.3 | 103.6 | 13.8 | 100.0 | 103.7 |
| 12 | 13.9 | 13.9 | 100.0 | 14.8 | 106.6 | 14.7 | 106.0 | 100.8 |
| 13 | 13.4 | .......... | .......... | 13.9 | 104.1 | 13.7 | 103.3 | 101.3 |
| 14 | 13.4 | .......... | .......... | 12.6 | 93.8 | 14.0 | 104.7 | 90.0 |
| 15 | 13.5 | .......... | .......... | 14.8 | 109.9 | 14.0 | 103.7 | 106.0 |
| 16 | 13.8 | .......... | .......... | .......... | .......... | 14.0 | 101.0 | .......... |
| 17 | 13.6 | .......... | .......... | .......... | .......... | 13.8 | 101.5 | .......... |
| Average ratio | .......... | .......... | 99.9 | .......... | 102.7 | .......... | 102.9 | 100.3 |

REFEREES 0.49, ELLIOTT 1.20, HINMAN-JENKINS 0.65 CUBIC FOOT PER HOUR

| Test | Referees No. 1 | Referees No. 2 | Ratio Ref. 2 to Ref. 1 | Elliott | Ratio Elliott to Ref. 1 | Hinman-Jenkins | Ratio H-J to Ref. 1 | Ratio Elliott to H-J |
|---|---|---|---|---|---|---|---|---|
| 18 | 15.2 | .......... | .......... | 14.9 | 98.0 | 14.3 | 94.0 | 104.1 |
| 19 | 13.9 | .......... | .......... | 14.0 | 101.0 | 13.0 | 93.6 | 107.8 |
| 20 | 14.3 | .......... | .......... | .......... | .......... | 13.3 | 93.0 | .......... |
| 21 | 15.4 | .......... | .......... | .......... | .......... | 14.4 | 93.5 | .......... |
| 22 | 13.1 | .......... | .......... | 13.1 | 100.0 | 12.9 | 98.5 | 101.7 |
| 23 | 13.2 | .......... | .......... | .......... | .......... | 12.2 | 92.5 | .......... |
| Average ratio | .......... | .......... | .......... | .......... | 99.7 | .......... | 94.2 | 104.4 |

REFEREES 0.50, ELLIOTT 1.20, HINMAN-JENKINS 0.50 CUBIC FOOT PER HOUR

| Test | Referees No. 1 | Referees No. 2 | Ratio Ref. 2 to Ref. 1 | Elliott | Ratio Elliott to Ref. 1 | Hinman-Jenkins | Ratio H-J to Ref. 1 | Ratio Elliott to H-J |
|---|---|---|---|---|---|---|---|---|
| 24 | 13.8 | .......... | .......... | 15.0 | 108.5 | 13.9 | 100.7 | 107.9 |
| 25 | 10.3 | .......... | .......... | 9.9 | 96.0 | 9.9 | 96.0 | 100.0 |
| 26 | 16.1 | .......... | .......... | 16.6 | 103.0 | .......... | .......... | .......... |
| 27 | 13.5 | .......... | .......... | .......... | .......... | 13.9 | 102.6 | .......... |
| 28 | 11.6 | .......... | .......... | .......... | .......... | 12.1 | 103.9 | .......... |
| 29 | 13.2 | .......... | .......... | .......... | .......... | 13.0 | 98.3 | .......... |
| Average ratio | .......... | .......... | .......... | .......... | 102.5 | .......... | 100.3 | 103.9 |

These data of Tables 1 and 2 showed that the two models of Referees apparatus agreed with each other very well, and therefore that the difference in size of these two condensers has no appreciable effect upon the experimental results. On the other hand, the Hinman-Jenkins and the Elliott apparatus, while agreeing with each other, almost always give results somewhat higher than those obtained with the Referees apparatus. These differences could be ascribed only to a difference in the efficiency of the condensation of the sulphur oxides, and the exact cause of this difference was the next point considered.

### (b) EFFICIENCY OF CONDENSATION

Three important factors affecting the efficiency of condensation of the sulphur in the products of combustion were considered, viz, the amount of condenser surface, the rate of burning of the gas, and the alkalinity of the atmosphere in the condenser chamber.

*Size of Condenser.*—The two makes of Referees apparatus used differed in size mainly in the condenser chamber, which was 25 per cent larger in the one than in the other case. As shown in Tables 1 and 2, these two models give results in very good agreement with each other. It is, therefore, certain that differences in size of condensers such as were used in this case have little effect upon the results.

As no cause was apparent for the lower results obtained with the Referees than with the other apparatus, except possible losses of sulphur with the products of combustion, tests were made upon the escaping gases to detect if possible sulphur dioxide or sulphur trioxide. The products were passed over the surface of a solution of barium chloride, hydrochloric acid, and bromine, but no precipitate of barium sulphate could be detected after passing all the products of burning for three hours over such solution. Although no sulphur could be found in the products by this method, it was decided to increase the condenser capacity of the Referees apparatus by adding a second bead tower at the top of the first; this practically doubled the size of the condenser. The condensed liquid from the two towers was collected and the sulphur determined independently in order to determine the amount of sulphur which ordinarily escaped from the single

tower. The results of these tests, as given in Table 6, show that about 1 to 3 per cent of all the sulphur was condensed in the extra tower, and it is probable that about this amount of sulphur escaped uncondensed from the apparatus as regularly operated. This loss, therefore, accounts for the lower results obtained with this apparatus, and it indicates the necessity of a larger condenser or modified method of operation for the Referees form of apparatus if great accuracy of test is required.

The Elliott apparatus, which has much more condensing surface than the Referees could be safely operated at higher rates of gas consumption. This point will be discussed in the next section.

*Amount of Gas Burned.*—The effect of varying the rate at which the gas was burned, shown in Table 2, is still better indicated in Table 3, which shows the percentage of sulphur condensed in each tower of the Elliott apparatus with the gas burning at three different rates. In every case the sulphur condensed in the trumpet tube is combined with that collected in the first tower. The significance of the results appears at once when we remember that the first tower with its connections is practically a large Referees apparatus and the sulphur which passes into the second tower is practically all lost in the Referees form.

It appears that there is a certain rate of combustion for each apparatus beyond which the loss of sulphur becomes serious. From our experiments we believe that if the ammonium carbonate or hydroxide is renewed as frequently as recommended later, 1.0 cubic foot per hour for the Elliott and 0.5 cubic foot for the other forms of apparatus are safe rates. The losses increase rapidly at higher rates.

## TABLE 3

### Amount of Sulphur Condensed in Different Parts of the Elliott Apparatus at Different Rates of Gas Consumption

| Rate (cubic feet per hour) | Sulphur in first tower (grains per 100 cubic feet of gas) | Sulphur in second tower (grains per 100 cubic feet of gas) | Total sulphur (grains per 100 cubic feet of gas) | Per cent of total condensed in second tower | Referees burned at 0.5 cubic foot per hour (sulphur, grains per 100 cubic feet of gas) |
|---|---|---|---|---|---|
| 1.36 | 5.7 | 3.7 | 9.4 | 39 | 15.5 |
| | 8.2 | 4.7 | 12.9 | 36 | 14.2 |
| | 4.9 | 1.5 | 6.4 | 23 | 11.5 |
| 1.20 | 13.9 | 1.1 | 15.0 | 8 | 13.8 |
| | 9.4 | 0.5 | 9.9 | 6 | 10.3 |
| | 14.8 | 1.8 | 16.6 | 8 | 16.1 |
| 0.9 | 11.5 | 1.7 | 13.2 | 1 | 13.7 |
| | 10.4 | 3.9 | 14.3 | 3 | 12.8 |
| | 10.7 | 2.5 | 13.2 | 2 | 12.4 |
| | 12.1 | 1.6 | 13.7 | 1 | 13.6 |
| | 12.2 | 2.0 | 14.2 | 1 | 13.8 |
| | 13.1 | 2.1 | 15.2 | 1 | 15.0 |

Indeed the amount of sulphur condensed per hour in the Elliott apparatus was less when the gas was burning at the rate of 1.36 cubic feet than when burning at 1.20 cubic feet per hour.

*Alkalinity of Air in Condenser Chamber.*—Our work throughout indicated that the most serious source of error in any apparatus of this type is an insufficient or irregular ammonia supply.

Table 4 shows the effect of using in the Referees apparatus lumps of carbonate which had previously been used and which were, therefore, deeply incrusted with bicarbonate. As much ammonium carbonate was used in each case as would lie in the annular space about the burner. From the decrease in efficiency of condensation on long use of the carbonate, shown by the results of Table 4, it appears that a 10-hour run, using a single supply of carbonate, could hardly be expected to give more than 90 to 95 per cent or a 20-hour run more than 75 to 80 per cent of the sulphur burned.

## TABLE 4

### Effect of Using Old Ammonium Carbonate on Referees Apparatus

| Test | Previous use of carbonate | Length of run | Sulphur condensed with old carbonate (A) | Sulphur condensed with fresh carbonate (B) | Ratio of (A) to (B) |
|---|---|---|---|---|---|
| | *Hours* | *Hours* | *Grains* | *Grains* | *Per cent* |
| 30 | 6 | 6.5 | 7.0 | 14.0 | 50 |
| 31 | 6 | 6.5 | 11.5 | 14.9 | 77 |
| 32 | 6.5 | 6 | 9.5 | 13.9 | 78 |
| 33 | 6 | 6 | 11.0 | 13.6 | 81 |
| 34 | (⁶) | (⁶) | 5.1 | 16.8 | 30 |

⁶ No carbonate used.

Table 5 shows the effect of varying the ammonia supply to the Elliott apparatus upon the percentage of the total sulphur which escapes from the first tower and is collected in the second. Similarly, Table 6 shows the percentage of total sulphur collected in the added condenser of the Referees apparatus previously mentioned (p. 18), first, when nothing was added to this second condenser; second, when concentrated ammonium hydroxide was slowly dropped in at the top of the second condenser; and third, when a solution of hydrogen peroxide and ammonium hydroxide was added in the same way. The object of adding hydrogen peroxide was to see what effect an oxidizing substance would have upon the absorption of the sulphur dioxide; but from the results obtained this effect appears to be negligible. In each case the apparatus was run in the same manner as in previous determinations, burning gas at the rate of 0.49 cubic feet per hour, the only change being in the added condenser. With this added condenser the performance of the apparatus was equal to the best results obtained from the Elliott apparatus.

TABLE 5

Percentage of Total Sulphur Condensed in Second Tower of Elliott Apparatus Burning 1.2 Cubic Feet of Gas per Hour

| $(NH_4)_2CO_3$ renewed every 3 hours | $(NH_4)_2CO_3$ renewed every hour | Air supplied to apparatus bubbled through concentrated $NH_4OH$ |
|---|---|---|
| *Per cent* | *Per cent* | *Per cent* |
| 7.5 | 0.6 | 0.1 |
| 6.0 | 0.8 | ............................... |
| 8.0 | ............................... | ............................... |

TABLE 6

Percentage of Total Sulphur Condensed in Added Condenser of Referees Apparatus

| Nothing added to second condenser | $NH_4OH$ added to second condenser | $NH_4OH + H_2O_2$ added to second condenser |
|---|---|---|
| 1.0 | 3.6 | 1.2 |
| 1.1 | 2.2 | 2.3 |
| .8 | 0.9 | 2.0 |
| ............................... | ............................... | 1.0 |
| Average, 1.0 | 2.2 | 1.6 |

In this connection it may be well to call attention to the higher results shown in Table 8 obtained with the old-form Elliott apparatus when using ammonium carbonate around the burner, than when running in sodium carbonate at the top of the condenser. The difference is due to an alkaline atmosphere as compared with a condensing surface covered with an alkaline liquid.

(c) AMOUNT OF WASH WATER REQUIRED

The Referees' "Notification" for 1912 states: "The condenser is then to be flushed twice or thrice by pouring quickly into the mouth of it 40 or 50 cubic centimeters of distilled water." However, results of our tests reported in Table 7 indicate that the use of at least four portions of wash water is desirable.

In a large number of tests it was found that the chimney tube of the Elliott and Referees forms did not contain appreciable amounts of condensed sulphur; nor does the ammonium hydroxide vessel about the Hinman-Jenkins burner take up any sulphur. However, in all forms of apparatus the trumpet tube which forms the burner chamber must be rinsed out, since from 0.5 to 1.0 mg of sulphur condenses as sulphate on the walls of this portion of the apparatus.

### TABLE 7

#### Number of Washings Required to Collect Condensate

| Washings [7] | Percentage of total sulphur collected | | |
|---|---|---|---|
| | Elliott | Hinman-Jenkins | Referees |
| 2 | 95.7 | 97.4 | 96.2 |
| 3 | 98.1 | 99.0 | 98.2 |
| 4 | 99.5 | 99.8 | 99.2 |
| 5 | 100 | 100 | 100 |

[7] For the Elliott 100 cc portions of wash water were used, but for the other two forms 50 cc portions were employed. The total obtained by five washings is taken as 100 per cent.

### 2. APPARATUS WITH WATER-COOLED OR LIQUID CONDENSATION

The early form of Elliott apparatus used a water-cooled condenser (as shown in Fig. 3), and the Drehschmidt apparatus and all modifications of it condense the sulphur by bubbling the products of combustion through liquids. These two types of apparatus, especially the latter, differ so greatly in principle from the Referees and other forms which have air-cooled condensers that they can be best considered separately.

Table 8 gives a series of comparisons between the Referees and the two forms of Elliott apparatus.

## TABLE 8

### Comparison of the Referees and Two Models of Elliott Apparatus

| Test | Referees (sulphur per 100 cubic feet) | Old-form Elliott | | New-form Elliott | |
|------|------|------|------|------|------|
| | | Sulphur per 100 cubic feet | Ratio to Referees | Sulphur per 100 cubic feet | Ratio to Referees |
| | *Grains* | *Grains* | *Per cent* | *Grains* | *Per cent* |
| 6 | 7.3 | 2.9 | 40 | | |
| 7 | 8.4 | 3.9 | 46 | 9.2 | 109 |
| 8 | 8.4 | 3.3 | 40 | 9.8 | 116 |
| 9 | 8.2 | 2.5 | 30 | 8.5 | 104 |
| 10 | 7.9 | 8.4 | 106 | 7.8 | 99 |
| 11 | 7.9 | 8.3 | 105 | 8.2 | 104 |
| 12 | 8.0 | 8.0 | 100 | 8.3 | 104 |
| 13 | 8.4 | 8.1 | 97 | 8.7 | 104 |
| 14 | 15.5 | 15.8 | 102 | 15.9 | 103 |
| 15 | 13.9 | 14.5 | 104 | 14.8 | 106 |
| 16 | 13.7 | 12.2 | 90 | 13.2 | 96 |

For the first four comparisons the old form of Elliott was operated without ammonium carbonate or ammonium hydroxide, only sodium hydroxide being introduced at the top and allowed to run down over the condenser bulbs, but in the other seven comparisons ammonium carbonate crystals were used as with the Referees.

Although when using ammonium carbonate with the old-form Elliott results of satisfactory accuracy can be obtained, yet the fragility and inconvenience of form do not make it a desirable apparatus for general use. As has been above indicated, its originator has been led to use the later model because of its greater convenience and strength.

The comparisons reported in Table 9 were made with the Referees and the original Drehschmidt. Only a few results were obtained, since the burner adjustment could be made with difficulty with the Drehschmidt apparatus, and on numerous trials the mixtures of gas and air in the burner chamber exploded or the flame was extinguished by lack of air. The apparatus was finally abandoned as being too inconvenient for general use.

The principle of condensation of the sulphur by bubbling the products of combustion through an alkaline liquid seems very

good, but for practical purposes the air-cooled condensers of the type of the Referees apparatus are sufficiently satisfactory; the latter type also does not require the use of suction. When used in a room where other gas is burning the apparatus of the Drehschmidt type has the advantage that the air entering does not carry in sulphur, but if the apparatus is properly used this factor is not serious.

### TABLE 9

#### Comparison of the Referees and Drehschmidt Apparatus

| Test | Referees (sulphur per 100 cubic feet) | Drehschmidt (sulphur per 100 cubic feet) | Ratio Drehschmidt to Referees |
|:---:|:---:|:---:|:---:|
| | *Grains* | *Grains* | *Per cent* |
| 1 | 16.1 | 17.2 | 107 |
| 2 | 16.6 | 16.8 | 101 |
| 3 | 15.7 | 15.5 | 99 |
| 4 | 15.9 | 13.4 | 84 |
| 5 | 15.5 | 12.9 | 83 |

The comparisons made between the Referees and the modified Somerville apparatus are reported in Table 10. No extended tests were made to determine the exact operating conditions which would be best to use, since this procedure is little used and is not particularly well adapted for works, use, or official testing.

### TABLE 10

#### Comparison of the Referees and Modified Somerville Apparatus

| Referees (sulphur per 100 cubic feet) | Modified Somerville (sulphur per 100 cubic feet) | Ratio Somerville to Referees |
|:---:|:---:|:---:|
| *Grains* | *Grains* | *Per cent* |
| 15.2 | 13.7 | 91 |
| 15.2 | 15.2 | 100 |
| 14.3 | 12.4 | 87 |
| 16.4 | 17.4 | 106 |
| 15.4 | 15.9 | 103 |
| 16.8 | 15.5 | 92 |
| 14.3 | 14.4 | 101 |
| 15.7 | 14.9 | 95 |
| 15.5 | 15.1 | 97 |

## III. RECOMMENDATIONS AS TO FORM AND OPERATION OF APPARATUS

### 1. MERITS OF VARIOUS APPARATUS

As has already been said, the methods in which the sulphur compounds are reduced to hydrogen sulphide and those in which oxidation of the sulphur is accomplished by a liquid are not sufficiently accurate except possibly for works control. They seem to have no particular advantages even in speed, since the Somerville method when properly carried out is the most rapid of all and considerably more accurate than the two groups just mentioned. However, use of the Somerville apparatus requires considerable skill and chemical knowledge, and the method is not as generally practicable as other methods.

Only the apparatus of the Referees or the Drehschmidt type seem reasonably satisfactory for general use in official testing of gas, but there is some difference of opinion as to the relative merits of the apparatus of these two groups. The apparatus with air-cooled condensers (Referees, Hinman-Jenkins, and Elliott) are most often used, being simpler, less fragile, and more convenient for frequent use; but the forms of apparatus in which the sulphur is condensed by a liquid reagent seem to give greater surety of complete condensation, and the usual forms of this group (Drehschmidt and its modifications) can be adapted for the purification of the air entering, so that no sulphur is introduced by it. For scientific use, where accuracy is of first importance, the Drehschmidt type would have considerable advantage; but for commercial work this increase in accuracy is not necessary. In fact it is more than overbalanced by the greater inconvenience of the apparatus as compared with the forms of the Referees type.

If an apparatus of the Referees type be desired, as will usually be the case, there are three common forms from which selection can be made, viz, Referees, Elliott, and Hinman-Jenkins. Each of these three has its peculiar advantages, and it is not possible to combine all of these in any one composite apparatus, nor is one of the three superior to the other two for all purposes.

For use in traveling inspection work the Hinman-Jenkins apparatus is certainly most convenient, since when taken down it can be packed in a very small case and is then easily portable. It is also somewhat more satisfactory in that the condensation of sulphur by the ammonium hydroxide used in it seems to be more certain and perfect than by ammonium carbonate. However, this advantage is lost unless fresh ammonia is added frequently. This frequent addition of ammonia (every 20 to 30 minutes) makes this apparatus less convenient than that of the Referees or Elliott, since it can not be left to run unattended for such long periods as those.

When the gas is burned at 1.0 to 1.2 cubic feet per hour in the Elliott apparatus, it is possible to get a full test within one and one-half or two hours of the beginning of the test. This is perhaps the most rapid-working apparatus of the three, but it requires a larger bulk of wash water, and it is also rather large and clumsy. The increase in size over the Referees form is a distinct advantage if a rapid rate of burning of the gas is desired, but it is not at all certain that in the end anything is gained by this increase in rate.

The Referees apparatus is most often used in gas testing in this country, and on this ground alone has some advantage for official use, since a result obtained with a form of apparatus in very general use is more generally accepted than a result from another form less well known. This general use of the Referees apparatus has been justified by its simplicity, convenience, and accuracy; and, although the accuracy obtainable with this as well as with other forms has often been overestimated, yet the results are quite satisfactory for all commercial or official work if reasonable care is observed in the selection and operation of the instrument.

### 2. PRECAUTIONS IN SELECTION OF APPARATUS

The observance of a few simple precautions in selection of the apparatus will perhaps prevent great inconvenience or even serious error in later work. It is therefore desirable to call attention here to a few of the most frequent difficulties in order that they may be avoided more easily.

*Hinman-Jenkins.*—This form of apparatus is supplied as far as we know by only one apparatus company [8] and is made by them to correspond very well with the original specifications. The dimensions of the various parts are given in the description and the apparatus is illustrated in an earlier section of this paper (p. 10). We recommend that the original form be followed exactly, since this has been found by us, as well as by several State inspectors, to be very satisfactory. However, it would be preferable to have the beads used in the condenser solid and not perforated, since the washing of the latter form is necessarily less efficient; and the bead jar should be filled to within 1 inch of the top with these beads (it is often only half filled). The burner should give a clean-cut blue flame and when burned at ordinary pressure (1.5 to 2.5 inches of water) should pass about 0.5 cubic foot of gas per hour. The proper adjustment of the burner is important, since otherwise incomplete combustion of the gas may result from leakage of the gas unburned from the air holes at the base of the burner.

*Referees.*—The description and figure of the Referees apparatus previously given do not give exact dimensions of the apparatus, for the reason that the different makers are supplying apparatus of somewhat different sizes, all of which will be satisfactory if within the limits set in this description. However, some of the essential points on which difference in form makes real difference in the convenience or reliability of the apparatus may be indicated. The trumpet tube must not be connected with the condenser by a rubber adaptor or stopper; the form of cork stopper previously indicated is very easily adjusted and is satisfactory. (See p. 6.) If a lead or other metal plate is furnished as a support for the marbles, it should be replaced by a glass rod bent into S shape. The drip tube should extend up into the base of the condenser about one-sixteenth of an inch, in order to keep a layer of liquid over the rubber stopper at the bottom.

*Elliott.*—The most recent form of apparatus described by Dr. A. H. Elliott [9] should be slightly modified by sealing the trumpet tube to the U tube connecting with the first condenser, since a rubber joint at this point introduces great liability to error. The

[8] L. E. Knott Apparatus Co., 15 Harcourt Street, Boston, Mass.
[9] Described above, as given in a private communication to the Bureau of Standards.

burner may be an ordinary metal Bunsen burner or, as described by Dr. Elliott, a porcelain Bunsen burner. The latter is cleaner and more attractive in appearance, but is fragile, expensive, and less likely to be so well made as to burn only 1 cubic foot of gas per hour without striking back when the flame is nonluminous. As is shown by the Referees burner, a metal burner can be used with entire satisfaction, and this is true even when no lava tip is used. The dimensions given previously (p. 8) are those of the originator's selection; if a smaller apparatus is desired it can easily be used, but the rate of burning the gas would then need to be reduced.

### 3. DIRECTIONS FOR SETTING UP OF APPARATUS.

If any form of apparatus except that of the Drehschmidt type is used, it is necessary for accurate work that it be set up in a room where no other gas is being burned in order that the air entering the apparatus may be free from sulphur. This will ordinarily cause no inconvenience. The apparatus can be readily set up in the office room of the inspector instead of in the chemical laboratory, since a simple gas connection is the only piping needed and the operation of the instrument need cause no objectionable dirt or odor.

The apparatus consists of pressure governor, U-water gauge, meter, and sulphur apparatus, these being connected in the order given. If the gas used for the sulphur test is also used for the ammonia test, the ammonia absorber is connected between the source of gas supply and the pressure governor. For connecting the various parts of the apparatus rubber tubing is not satisfactory for two reasons. First, the rubber can absorb and give up sulphur from and to the gas according to the quantity of sulphur in the gas and the temperature; and, second, the rubber tubing soon becomes hard and is much more apt to leak than is a metal or a glass tube. It is most convenient usually to make the connections from governor to gauge, gauge to meter, and meter to burner permanent; these can be of glass tubing with rubber connections wired on, except the connection of meter to burner. For the latter it is best to solder a metal tube to the burner inlet (about 6 to 8 inches is a convenient length), so that if the burner strikes

back during a test the connection is not broken at the base of the burner and gas allowed to escape or take fire at this point. Especially for long runs, when no one is in the room for a long time during the test, such a connection is much safer than one of rubber.

The meter and governor used may be either of the wet or dry type. The usual precautions as to leveling and proper adjustment should, of course, be observed. The pressure on the governor should be so adjusted once for all that when the gas is turned on full at the supply cock the burner will pass gas at the desired rate.

The connection between meter and burner, as well as the meter itself, should be frequently tested to show the absence of leaks. Any leaks, even very small ones, may cause appreciable errors in the test, since the rate of gas consumption is small.

### 4. METHODS OF OPERATION RECOMMENDED

After all connections and adjustments of the apparatus have been made the gas should be burned from the apparatus for several hours to saturate the meter and governor water and to purge the connections. Before each test the line may be purged in this way by burning the gas for about a half hour, a burner which will pass 5 cubic feet or more per hour being substituted for the regular test burner.

When the line is thus purged, the regular burner is put in place and ammonia or ammonium carbonate placed on the burner; for the Referees and Elliott apparatus as much ammonium carbonate is used as will find place about the burner pillar, and for the Hinman-Jenkins about 10 cc of strong ammonia solution is used. The ammonium carbonate should be in large lumps which have been freed from efflorescent portions.

It is usually desirable to rinse out condenser and chimney tubes just before starting the test, in order to prevent dust which might have collected there between tests contaminating the condensate. This also prevents loss of sulphur from the dry condenser during the first few minutes. When all parts, including the flask to collect the condensate are in place, the trumpet tube is set over the burner and quickly connected with the condenser, the meter read-

ing being noted at the instant the trumpet tube is put in place. This reading and the time, meter temperature, barometer, and manometer readings are recorded in the test record book.

The gas being burned at one-half cubic foot per hour in the Referees or Hinman-Jenkins or 1 foot in the Elliott apparatus, the test can be continued for any desired period, the ammonia or ammonium carbonate being renewed, as indicated below. If the sulphur in the condensed liquid is to be determined by means of a turbidimeter (see a later section of this paper), it is necessary to burn the apparatus only two hours. In this event it is not necessary to renew the ammonium carbonate for either the Elliott or Referees apparatus; but in this or any other test about 3 or 5 cc of fresh ammonia solution must be added to the Hinman-Jenkins apparatus every 20 minutes.

If the sulphate is to be determined gravimetrically, it is generally desirable to burn at least 2½ or 3 cubic feet of gas for a test. However, there is no need for burning 10 feet, as usually is done, since the gravimetric method is sufficiently accurate on the sulphur from 2.5 feet of ordinary coal gas or water gas to give no error as great as the irregularities of condensation in the apparatus. These are not appreciably lessened by longer runs. The advantage of burning the gas over a long period in order to get a so-called "better average sample of the gas" is much overestimated. With the ordinary uniformity of works operation and a single coal supply, changes in the sulphur content of the gas from day to day are very small. For this reason a short test will usually give as fair a sample of the full day as one taken over a long period.

When it is desired to burn more than 3 cubic feet of gas for a test, it is necessary to replenish the supply of ammonium carbonate on both the Elliott and the Referees' apparatus. To do this the gas is shut off and the trumpet tube allowed to cool so that it may be handled comfortably. A fresh supply of carbonate is then added, the burner relighted, and the trumpet tube replaced quickly. If more than a very few thousandths of a cubic foot of gas are burned with the trumpet tube off, the amount so burned should be deducted from the total used for the test. A fresh supply of carbonate must be added in this manner after every 3

feet of gas burned in either the Referees or Elliott apparatus; with the Hinman-Jenkins apparatus ammonia is added every 20 minutes.

When sufficient gas has been burned, the supply is cut off and the apparatus allowed to cool. The trumpet tube is then washed once and the condenser four times. For the Referees and Hinman-Jenkins apparatus each portion of wash water is 50 cc and is added all at once to thoroughly flush the condenser; with the Elliott form 100-cc portions of water are used, the last two portions used in the second tower being subsequently used as the first two portions for the first tower. In this way the wash water is kept at reasonable bulk. The time, meter reading, meter temperature, and barometer are recorded again at the close of the test.

The sulphate in the condensed liquid and wash water is determined by one of the methods given in a later section of this paper. From sulphate found and corrected volume of gas burned, the sulphur content of the gas (in grains of sulphur per 100 cubic feet of gas) is calculated.

## IV.—DETERMINATION OF SULPHATE IN THE SOLUTIONS OBTAINED

In all the forms of apparatus described, the suplhur is obtained in solution in the form of sulphates and, except in the case of the Somerville procedure, it is this sulphate which must be determined. The oxidation from sulphites to sulphates is accomplished in the Drehschmidt and Somerville types of apparatus by an oxidizing agent, usually bromine or iodine, in the absorption liquid; and in the other forms of apparatus it is accomplished by the action of the oxygen in the hot products of combustion on the alkaline solution of sulphite formed in the condenser.

Numerous determinations were made of the sulphites present in the condensate from the various forms of apparatus and, while it was nearly always possible to get a qualitative test for sulphites, the amount was never found to be in excess of two-tenths of a per cent of the total sulphur present. It is, therefore, a negligible amount in a determination of this kind.

The methods of determining the sulphate which are available for use for this work are of three kinds—gravimetric, volumetric, and turbidimetric. The procedure used for most of the comparisons described in the previous sections was the first gravimetric method described below (practically the one recommended by Johnston and Adams;[10] but for some of the comparisons of Table 10 the turbidimetric procedure was followed.

In the following sections four methods are given which have been tried out with solutions of the character obtained from the Referees type of apparatus, together with a short series of comparisons which shows that they are sufficiently accurate for this kind of work.

### 1. METHOD I—GRAVIMETRIC, WITH EVAPORATION TO DRYNESS

Dilute or evaporate the portion of liquid taken for analysis to about 300 cc, add 50 cc of concentrated hydrochloric acid, heat to boiling, then run in 10 cc of 10 per cent barium chloride solution through a tube or from a burette, delivering it at the rate of about 8 to 10 cc per minute, stirring constantly during the addition. After evaporation to dryness on the steam bath, take up with 75 to 100 cc of hot water, filter through a good, close-grained paper, and wash with hot water until the bulk of the filtrate and washings amounts to 200 cc. In a weighed platinum crucible char the paper with a low Bunsen flame and finally ignite until the precipitate appears white. Cool the crucible in a desiccator and weigh.

The precipitate now contains a small amount of silica, which may cause an error of 0.1 to 0.4 grain per 100 cubic feet in the apparent amount of sulphur in the gas. Bearing this source of error in mind, it is only necessary to correct for it when the amount of sulphur exceeds the legal limit by a small amount. The correction is easily made by moistening the precipitate with a drop of hydrofluoric and then one of sulphuric acid, drying, igniting, and weighing again. The silica is all removed by this operation.

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[10] J. Amer. Chem. Soc., **33**, pp. 829–845; 1911.

### 2. METHOD II—GRAVIMETRIC PRECIPITATION IN NEARLY NEUTRAL SOLUTION

In the more common procedures for the gravimetric sulphate determination, the precipitation of the barium sulphate is made in nearly neutral solution. This method was used by us as follows:

To the solution which is diluted or concentrated to about 300 cc, add 2 or 3 drops of methyl-orange or p-nitrophenol solution[11] and neutralize with hydrochloric acid, adding this solution dropwise; and finally add 2 cc of the 1 : 1 acid in excess. Heat to boiling, add 10 cc of 10 per cent barium chloride solution, boil five minutes, allow to stand on a steam bath for a half hour or longer, filter, wash, ignite, and weigh the barium sulphate as in Method I. The precipitation when always made in the presence of a fixed amount of acid is affected always in equal degree by the solubility of the barium sulphate in the acid. Under the conditions given the loss from this source is negligible for the present work.

### 3. METHOD III—VOLUMETRIC

A number of volumetric methods have been recommended for the determination of sulphates, several of which are suitable for use with the liquids obtained from the Referees' and Hinman-Jenkins apparatus. Only one of these, a modification of that recommended by Holliger,[12] will be described.

Make up a solution of 50 g $BaCl_2.2H_2O$ per liter, and one of 30.5 g $K_2Cr_2O_7$ per liter. To 300 cc of water add 10 cc of 1.1 hydrochloric acid and exactly 15 cc (from pipettes) of each of the above solutions; heat to boiling, add two or three drops of a dilute solution of ferric chloride, then slowly add 10 per cent ammonium hydroxide until a precipitate forms, which does not redissolve on stirring. Add 5 cc of the ammonia solution in excess, boil five minutes, filter and wash thoroughly with hot water. Allow the filtrate to cool, acidify with hydrochloric acid, add 2 grams of solid potassium iodide, or a solution containing that amount, and titrate with tenth normal sodium thiosulphate, using starch as an indicator. The amount of thiosulphate solution used in this
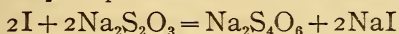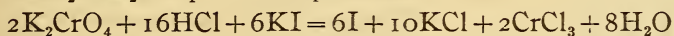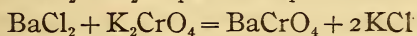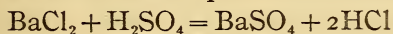
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[11] Any other indicator sensitive to ammonia, but not affected by carbon dioxide, may be used.
[12] Zs. anal. Chem., **49**, p. 84; 1910.

blank is to be subtracted from the amount used in each subsequent determination.

To make a determination of the sulphate in a solution, dilute or concentrate the sample taken to 300 cc, add 10 cc of 1.1 hydrochloric acid, heat to boiling, add 15 cc of barium chloride solution from the pipette used in the blank test, boil five minutes, add 15 cc of potassium bichromate solution and a few drops of ferric chloride, precipitate with ammonium hydroxide, and complete the determination exactly as in the blank test. From the amount of thiosulphate solution used subtract the amount required in the blank. The remainder represents the sulphate in the sample taken.

The reactions upon which the method is based are:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$
$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$$
$$2K_2CrO_4 + 16HCl + 6KI = 6I + 10KCl + 2CrCl_3 + 8H_2O$$
$$2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

From the above equations it will be seen that three $Na_2S_2O_3$ are equivalent to one S; hence 1 cc of tenth-normal thiosulphate solution is equivalent to 1.069 mg (0.0165 grain) of sulphur.

The above method was selected in preference to other methods previously used, which have been open to the following objections:

1. In those using a hydrochloric acid solution of barium chromate the reducing action of the acid on the chromate has introduced serious errors.[13]

2. In those which use exactly equivalent amounts of barium chloride and potassium bichromate, it is somewhat difficult to make the solutions of exactly the right strength and a blank test must be made.[14]

3. The use of a suspension of barium chromate or of the solid is less convenient than that of solutions and since it is sometimes difficult to obtain the barium salt free from alkali chromate a blank test should also be made with this method.[15]

[13] Andrews: Am. Chem. J., **11**, p. 567; 1889. Pennock: J. Am. Chem. Soc., **26**, p. 1265; 1903. Holliger: Zs. anal. Chem., **49**, p. 84; 1910. Bradley: Chem. Eng., **13**, p. 26; 1911. Reuter: Chem.-Ztg., p. 357; 1898.
[14] Roemer: Zs. anal. Chem., **49**, p. 490; 1910. Precht: Zs. anal. Chem., **18**, p. 521; 1879.
[15] Bruhns: Zs. anal. Chem., **45**, p. 573; 1906. Kowarowsky: Chem.-Ztg., p. 498; 1907.

4. In all methods, the solubility of the barium chromate should be taken into account.

All of these sources of error or difficulty are taken care of by a single blank test, when the chromate solution is slightly stronger than the barium chloride solution, as in the method described. The solubility of barium chromate is somewhat affected by the concentration of ammonium chloride and of ammonium hydroxide in the solution; but by having the same bulk of solution, adding the same amount of hydrochloric acid, and precipitating in the same manner in the blank as in the determination, the effect of this source of error is also eliminated. The use of a small amount of ferric chloride, as recommended by Holliger (loc. cit.), aids greatly in collecting the precipitate of $BaCrO_4$ and $BaSO_4$ for the filtration.

### 4. METHOD IV—TURBIDIMETRIC

An investigation to determine the suitability of the turbidimeter[16] as a means of estimating sulphur in the solutions from the Referees apparatus, and the effect of varying certain conditions was undertaken. In all, about 300 determinations were made. The turbidimeter used is shown in Fig. 9. It consists of a cylindrical glass tube graduated from the bo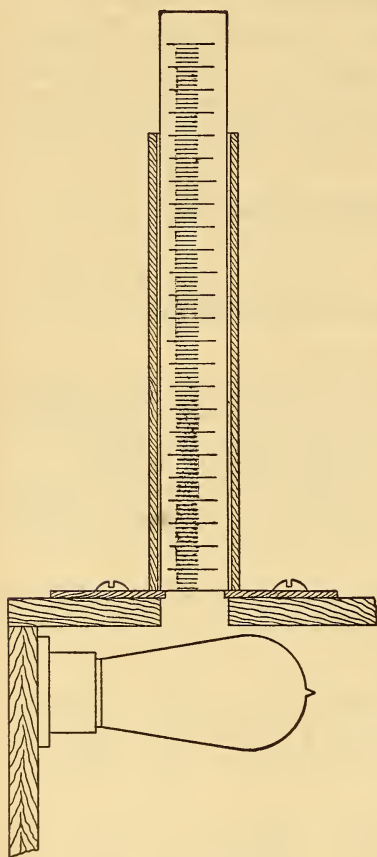ttom in centimeters, surrounded and held in place above the light by a brass tube. The light used was in most cases a 16-candlepower carbon filament lamp, so placed that a straight portion of the filament extended diametrically across just below the bottom of the tube.



Fig. 9.—*Turbidimeter*

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[16] Hinds: J. Am. Chem. Soc., **18**, p. 661, 1896; **22**, p. 269, 1900; **24**, p. 848, 1902.

For each determination the sulphate is precipitated with barium chloride and the solution stirred vigorously until precipitation appears to be complete. It is then poured into the tube until the filament entirely disappears, the depth of solution required to cause this disappearance being a measure of the amount of sulphate in the solution.

Since little was known of the effect of different conditions of operation on the result of the tests, a number of special comparisons were made, the results of which are given in the following paragraphs.

The incandescent filament gives a sharper end point than any other source of light so far devised.[17] It is not affected by drafts, does not smoke or crack the tube, and can be conveniently placed under a table or in another out-of-the-way place. A series of comparisons, using the incandescent filament, the standard candle, and the 0.5 mm slot recommended by Leighton (loc. cit.), is given in Table 11. In each case the same liquid was used with each source of light in turn. It can be seen that the three light sources give excellently agreeing results.

TABLE 11

Comparison of Results with Different Lights in Turbidimeter

| Incandescent filament | | Candle | | Electric light below a 0.5 mm slot | |
|---|---|---|---|---|---|
| Depth of solution | Milligrams of sulphur per 100 cc | Depth of solution | Milligrams of sulphur per 100 cc | Depth of solution | Milligrams of sulphur per 100 cc |
| 24.0 | 1.13 | 25.0 | 1.12 | 25.0 | 1.12 |
| 20.3 | 1.22 | 20.6 | 1.21 | 20.4 | 1.22 |
| 12.3 | 1.77 | 12.3 | 1.77 | 12.2 | 1.79 |
| 11.6 | 1.86 | 11.8 | 1.85 | 11.6 | 1.86 |
| 8.5 | 2.48 | 8.5 | 2.48 | 8.4 | 2.51 |
| 7.2 | 2.93 | 7.0 | 3.01 | 7.2 | 2.93 |
| 5.9 | 3.60 | 6.1 | 3.50 | 5.9 | 3.60 |
| 5.4 | 3.95 | 5.4 | 3.95 | 5.2 | 4.09 |
| 4.1 | 5.25 | 4.1 | 5.25 | 3.9 | 5.55 |
| 3.7 | 5.93 | 3.8 | 5.77 | 3.7 | 5.93 |
| 3.4 | 6.50 | 3.5 | 6.26 | 3.3 | 6.70 |

[17] See Jackson: J. Am. Chem. Soc., 23, p. 799; 1901. Parr: J. Ind. Eng. Chem., 1, p. 689; 1909. Leighton, U. S. Geological Survey Water Supply and Irrigation Paper No. 151, p. 27; 1905.

See also H. F. Muer: J. Ind. Eng. Chem., 3, p. 553–7; 1911. This article reports an extended series of tests on the turbidimeter.

The effect of using different precipitants as proposed by various persons who have used the turbidimeter for sulphate determinations is shown in Fig. 10.   It will be observed that there is less



DIAGRAM SHOWING EFFECT OF
PRECIPITANT USED
UPON
SULPHUR TURBIDIMETER CURVE

PRECIPITANTS

+ SOLID $BaCl_2$
O 10% $BaCl_2$ SOLUTION.
● 10% $BaCl_2$ SOL. SAT. WITH $H_2C_2O_4$
x 10% $BaCl_2$ 0.1% $H_2C_2O_4$ SOLUTION.
$BaCl_2$ SOLUTION CONTAINS 50 G. $BaCl_2$ $2H_2O$
IN 450 CC

DEPTH IN CENTIMETERS

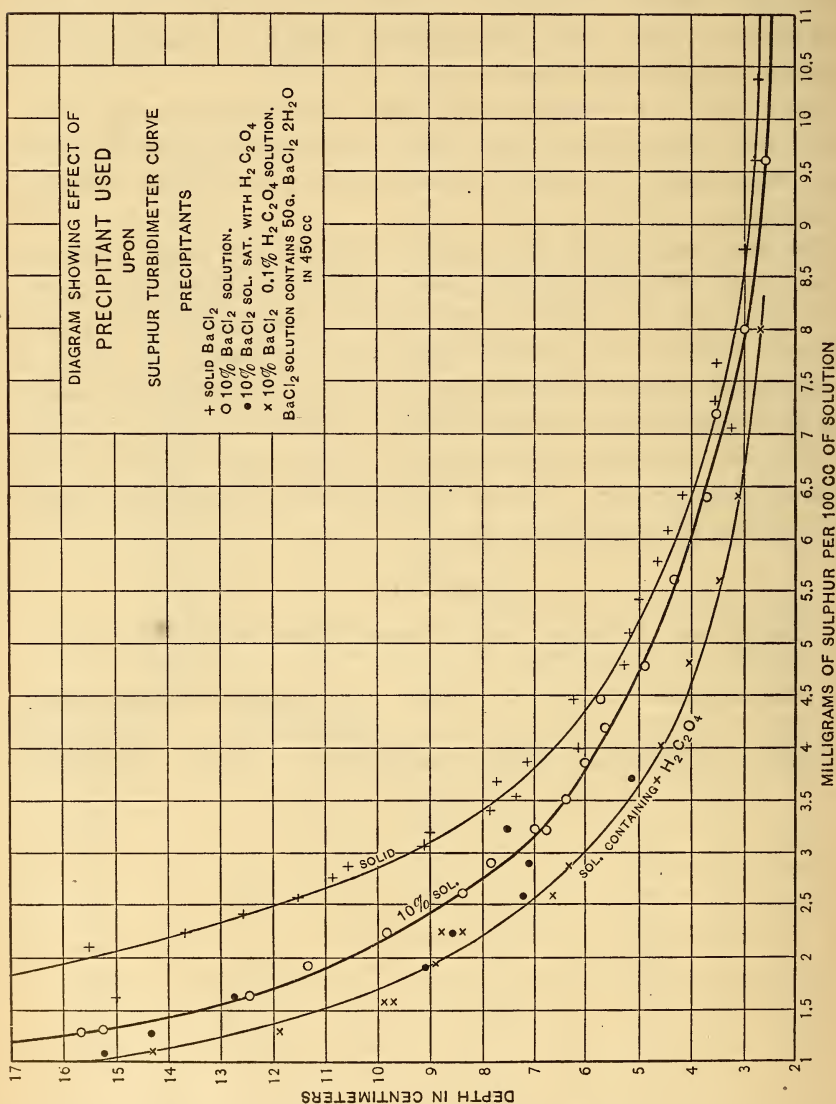MILLIGRAMS OF SULPHUR PER 100 CC OF SOLUTION

Fig. 10

variation where 10 per cent barium chloride solution is used than with other precipitants; the addition of oxalic acid gave a finer precipitate and a sharper end point, but successive determinations

were more discordant. Agreement of duplicates and certainty of result is most desirable in this method, since in any case the results are fixed by comparison with results on known amounts of sulphur. Variation of a single test from the average of all is therefore serious, but the shape of the calibration curves is not of influence, so long as regular and calibration tests are made in the same way.

Fig. 11 shows the effect of small amounts of hydrochloric acid upon the turbidimeter curve. Larger amounts caused much greater variations. Fig. 12 shows the effect of temperature of precipitation upon solutions of average strength. Fig. 13 is the curve drawn from the results obtained under the conditions of precipitation recommended below. Fig. 14 represents the same data as Fig. 13, with concentrations expressed in hundredths of a grain instead of milligrams.

The following method was finally adopted, and is recommended for use if it is desired to employ a turbidimetric procedure:

The condensate and washings from the sulphur apparatus are neutralized with hydrochloric acid,[18] then 2 cc of the 1:1 acid is added in excess. The solution is measured (to the nearest cubic centimeter) and a 90-cc portion placed in a small beaker for the test. It may be measured in an ordinary graduated cylinder if it is certain that the ratio of the small cylinder to the larger measuring vessel first used is correct. While the solution is between 25 and 30°, 10 cc of a 10 per cent solution of $BaCl_2.2H_2O$ is added and the whole stirred vigorously until the precipitation appears to be complete. (This usually requires less than one minute's stirring.)

The suspension is now poured into the clean and dry turbidimeter tube, a small portion at a time, until the filament of the lighted lamp disappears from view. After the first trial the solution is poured back into the beaker, stirred vigorously, and the observation of the point at which the filament disappears is repeated until this is fixed within 1 mm. During the time the solution is being added the portion remaining in the beaker should be kept well stirred, so that the small portions added from it will be representative of the whole bulk. The first time the solution is poured into the observation tube the latter must be dry and

[18] An indicator is required which is sensitive to ammonia but not to carbon dioxide. Para-nitro-phenol is the most satisfactory because it is colorless in acid solution.

clean.    In cleaning it care should be taken to remove, without scratching the tube, the film of sulphate which adheres so persistently to the bottom.



DIAGRAM SHOWING EFFECT OF
HYDROCHLORIC ACID
UPON
SULPHUR TURBIDIMETER CURVE
SOLUTIONS CONTAIN

$+ H_2SO_4$
● $(NH_4)_2 SO_4 + 1$ cc    1—1 HCl PER 100 cc
○ $(NH_4)_2 SO_4 + 2$ cc    1—1 HCl PER 100 cc
CURVE 1—SOLUTIONS OF $H_2SO_4$ FREE FROM HCl
CURVE 2—SOLUTIONS CONTAINING HCl

DEPTH IN CENTIMETERS

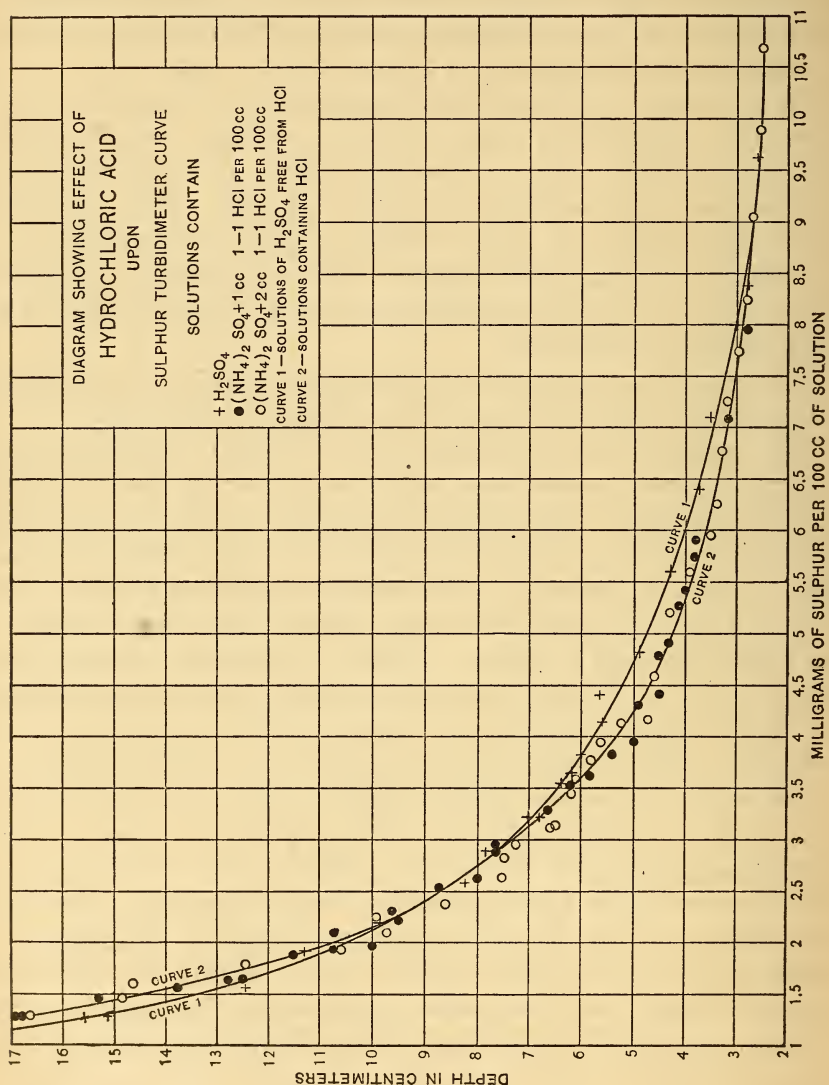MILLIGRAMS OF SULPHUR PER 100 CC OF SOLUTION

Fig. 11

Further tests on a second 90 cc of the original neutralized solution of sulphate should be made if considerable accuracy is needed. The amount of sulphur indicated by the curves of Figs. 13 and 14,

corresponding to the depth of liquid in the turbidimeter measurement, is multiplied by the number of cubic centimeters of neutralized condensate and divided by 90 (the volume of sample taken) to give the total amount of sulphur obtained by burning the gas.
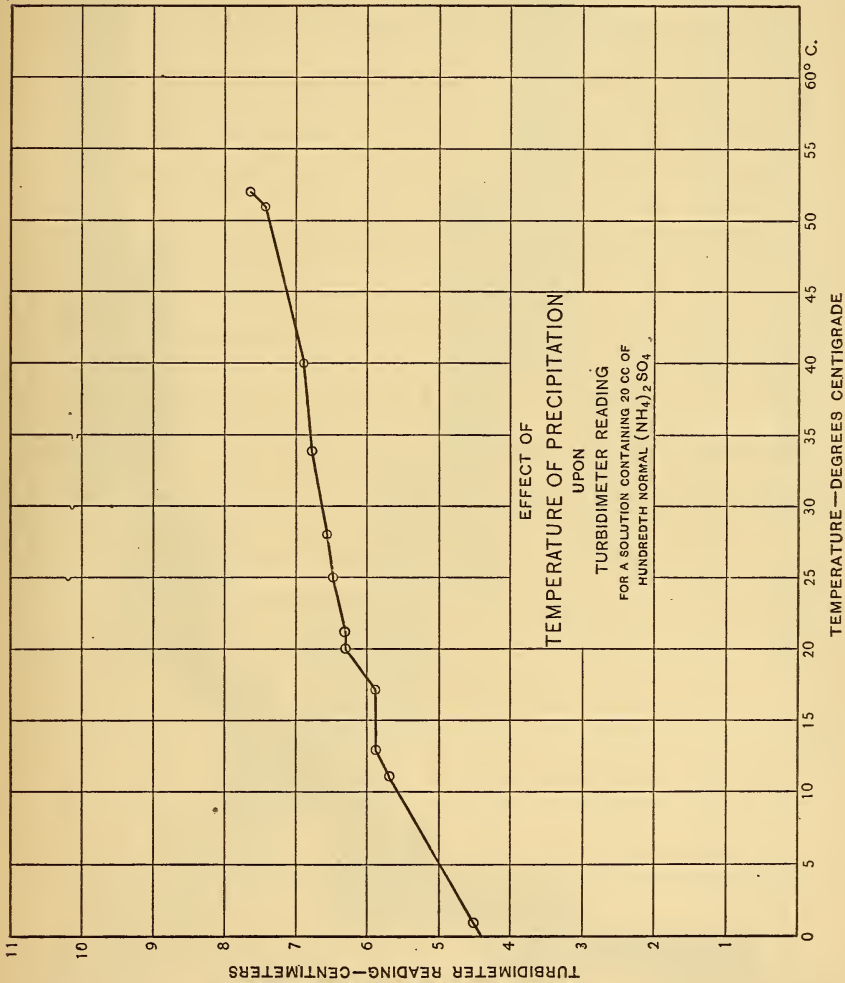


EFFECT OF
TEMPERATURE OF PRECIPITATION
UPON
TURBIDIMETER READING
FOR A SOLUTION CONTAINING 20 CC OF
HUNDREDTH NORMAL $(NH_4)_2SO_4$

TEMPERATURE—DEGREES CENTIGRADE

Fig. 12

TURBIDIMETER READING—CENTIMETERS

For convenience in this calculation the condensate after neutralization can be made up to 270 or 360 cc, and the observed values for the 90-cc portion are then multiplied by 3 or 4.

The curves of Figs. 13 and 14 may be used by any observer if care is exercised in following exactly the method given in the

preceding paragraph; the acidity and temperature limits must be particularly observed; the character of light used is less important. In any case it is well for an inexperienced observer to take
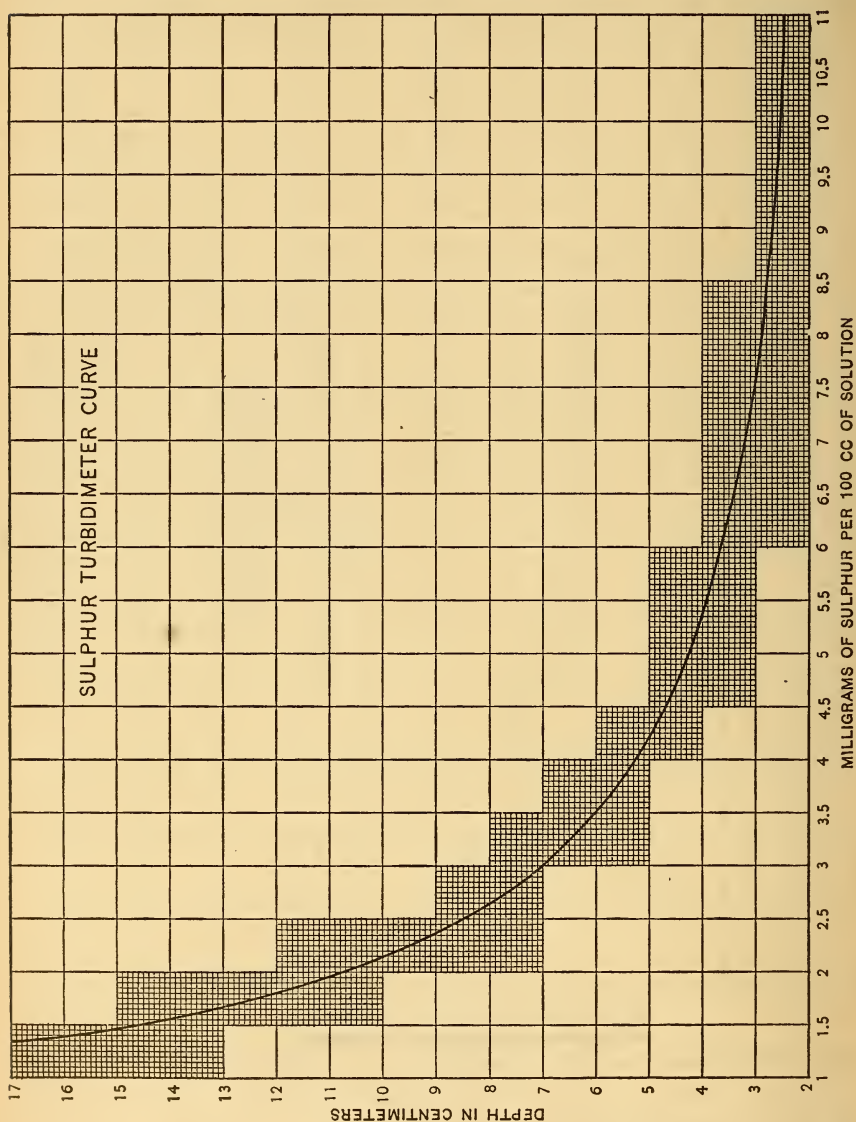


Fig. 13

known amounts of a standard sulphuric acid solution and run through the test until assured that his observations are consistent and correct.

To show the accuracy of the method as used, one series of tests from which our conclusions are drawn has been summarized in Tables 12 and 13. This summary shows the average and the
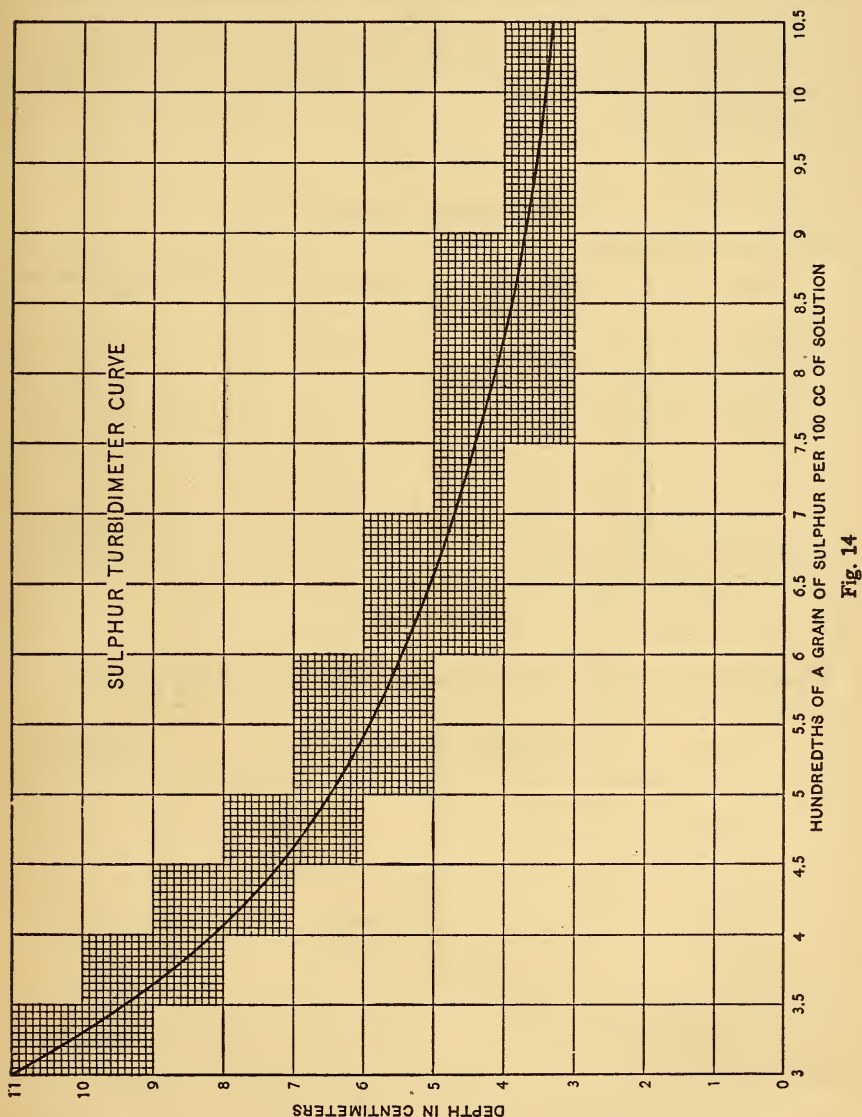


Fig. 14

maximum deviation of individual tests from the value calculated from the amount of standard sulphuric acid used—i. e., the errors which were found by making a single precipitation of barium sul-

phate and suitable observations on it. When more than one portion is precipitated and used for a determination, the accuracy would be materially increased, so that in tests on three portions of a solution the average of the three ought not to be much more than 1 per cent in error. It should be remembered that three tests can be made in this way much more quickly than a single test by any other method.

TABLE 12

Turbidimetric Errors

| Sulphur | Average error | Maximum error | Number of determinations |
|---------|---------------|---------------|--------------------------|
| *Mg per 100 cc* | *Per cent* | *Per cent* | |
| 1– 2 | 2.9 | 8.7 | 13 |
| 2– 3 | 3.5 | 7.1 | 13 |
| 3– 4 | 2.5 | 7.7 | 17 |
| 4– 5 | 2.6 | 6.3 | 8 |
| 5– 6 | 1.3 | 5.2 | 7 |
| 6– 8 | 2.6 | 5.6 | 7 |
| 8–11 | 3.4 | 6.3 | 5 |
| All values............ | 2.7 | 8.7 | 70 |

TABLE 13

Percentage of error in determinations between 2 and 8 mg per 100 cc

| Error | Number of determinations | Error | Number of determinations |
|-------|--------------------------|-------|--------------------------|
| *Per cent* | | *Per cent* | |
| 0.0–0.5 | 11 | 5.5–6.5 | 6 |
| 0.5–1.5 | 12 | 6.5–7.5 | 2 |
| 1.5–2.5 | 5 | 7.7 | 1 |
| 2.5–3.5 | 7 | Total...................... | 52 |
| 3.5–4.5 | 3 | | |
| 4.5–5.5 | 5 | | |

## 5. COMPARISON OF METHODS FOR THE SULPHATE DETERMINATION

For the present purposes it was sufficient to know that the several methods for the sulphate determination gave results agreeing within 1 per cent; but under the conditions of their use, on solutions containing considerable amounts of ammonium carbonate, it was not certain that this was the case. However, a number of comparisons which we have made show that the agreement of the four methods among themselves is satisfactory. All of the details of these tests are not given here; only sufficient data are included to show that these simple methods are suitable for our purpose.

### TABLE 14

Comparison of Methods for Sulphate Determination. Sulphur (Milligrams per Gram of Solution) in Standard $H_2SO_4$ Solution Determined by Different Methods in Presence of Excess of Ammonium Carbonate, except as Otherwise Noted

| Volumetric, against NaOH and benzoic acid | Gravimetric, method 1 | Gravimetric, method 2 | Volumetric, method 3 | |
|---|---|---|---|---|
| | | | Oxalate standard (no carbonate added) | $H_2SO_4$ standard |
| 1.589 | 1.591 | 1.597 | 1.602 | 1.595 |
| 93 | 91 | 93 | 1.597 | 1.602 |
| 90 | 90 | 92 | 1.600 | 1.597 |
| 92 | [19] 1.609 | 99 | 1.599 | 1.601 |
| 92 | 1.596 | 97 | 1.602 | 1.596 |
| 92 | 96 | 92 | ................... | 1.589 |
| 89 | 88 | 99 | ................... | 1.574 |
| 90 | 92 | 91 | ................... | 1.575 |
| ................... | 94 | 1.600 | ................... | ................... |
| 1.591 | 1.592 | 1.595 | 1.600 | 1.589 |

[19] Omitted from average.

The data of the above table show the results obtained under rather unfavorable conditions by the two gravimetric and the one volumetric method as compared with the correct values obtained for a standard sulphuric acid solution by a usual and accepted procedure. The results of the first set by method 3 are

calculated on the basis of the value of the thiosulphate solution obtained by titration against potassium permanganate, which was standardized with sodium oxalate. In the second series the thiosulphate was checked against the standard sulphuric acid itself; in this latter the tests were made in the presence of added ammonium carbonate. The values given were in some cases obtained on very small amounts of sulphate, from 6 to 30 mg of sulphur being present in the various test samples. The results are thus less precise than otherwise and do not give very fair credit to the method as far as its possible accuracy goes.

For accurate work the gravimetric methods are to be preferred, but for rapid work the turbidimetric and volumetric methods will serve very well, and, unless the test indicates that the sulphur is very near the permissible limit, they are probably sufficiently accurate for official use. The volumetric method is adapted especially for use in state inspection, where a large number of test solutions are collected in the field work and subsequently examined at the headquarters laboratory. In most cases, however, the turbidimeter, which is easily portable, may be carried with the inspector and a test made at the time the sulphate is collected, thus avoiding the necessity of transporting the solutions obtained to headquarters.

WASHINGTON, March 7, 1913.